Microstructure and Mechanical Properties of Ternary Phase Polypropylene/Elastomer/Magnesium Hydroxide Fire-Retardant Compositions

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SYNOPSIS

Fire-retardant polypropylene (PP) composites were prepared by combining this polymer with uncoated and surface treated forms of magnesium hydroxide filler and various elastomeric modifiers, with and without maleic anhydride functionalization. Mechanical properties of binary and ternary phase compositions differed significantly and are discussed in terms of their microstructures (determined principally by SEM and FTIR) and the relative interaction of the components. Impact strength, in particular, was strongly influenced by the presence of filler surface treatment and the degree of rubbery phase dispersion. FTIR showed that functionalized ethylene–propylene rubber (F-EPR) reacted with the surface of uncoated magnesium hydroxide leading to extensive rubber encapsulation and an improvement in toughness relative to unmodified EPR, which was present in the matrix only as phase dispersed droplets. However, by blending F-EPR with filler surface treated with magnesium stearate, encapsulation was inhibited and the rubber was preferentially dispersed in the PP matrix. This formulation resulted in both improved filler–matrix interaction and enhanced matrix toughening leading to a further increase in impact strength. The effects of material composition on melt flow behavior and UL94 flammability rating, are also reported. © 1996 John Wiley & Sons, Inc.

INTRODUCTION

The usefulness of polypropylene (PP) can be limited by its high flammability, a tendency to embrittle at temperatures below its glass transition temperature (between 0 and 6°C), and only modest stiffness, particularly at elevated temperatures.

Poor low temperature impact strength is generally overcome through copolymerization with ethylene, or by melt blending with incompatible rubbery materials, in particular ethylene–propylene copolymer (EPR) or ethylene–propylene–diene terpolymer (EPDM).[1] However, this improvement usually results in a reduction in other properties, including modulus and hardness.

In binary blends of PP with EPR or EPDM and natural rubber (NR), many reports have been published on the factors controlling the morphology of the rubbery component and crystalline microstructure of the thermoplastic. Particular consideration has been given to the size and size distribution of the disperse phase in relation to the viscosity ratio of the polymeric phases,[2–4] the effects of blend composition,[5,6] interfacial phenomena between the phases (in particular the effect of the rubber on crystallization of the PP[1,7–9]), and the importance of the blending procedure in defining morphology.[10,11]

Extensive analysis of their mechanical properties has also been carried out,[2,5,7,12–16] with particular emphasis on impact strength and fracture toughness, in order to provide a mechanistic explanation for the concept of rubber toughening. In general, the function of the rubber is to promote and control deformation in the matrix from localized points of

Table I   Formulation of PP Compositions

Sample	PP	Mg (OH)$_2$ (Lycal 96HSE)	Mg (OH)$_2$ (TP100)	F-EPR	EPR	ENR
	100	—	—	—	—	—
A	40	60	—	—	—	—
B	36.2	—	63.8	—	—	—
C	32.5	60	—	—	—	7.5
D	28.7	—	63.8	—	—	7.5
E	37.5	60	—	2.5	—	—
F	35	60	—	5.0	—	—
G	32.5	60	—	7.5	—	—
H	32.5	60	—	—	7.5	—
I	28.7	—	63.8	7.5	—	—
J	32.5	60	—	5.0	2.5	—
K	32.5	60	—	2.5	5.0	—

All values in wt %. PP, polypropylene; F-EPR, functionalized ethylene–propylene rubber; EPR, ethylene–propylene rubber; ENR, epoxidized natural rubber; Lycal 96HSE, uncoated magnesium hydroxide; TP100, Lycal 96HSE coated with 6% by weight of magnesium stearate.

stress concentration around the rubber particles, which in PP creates increased matrix yielding. It is known that the resulting increase in toughness is strongly dependent on rubber particle size.[17]

Incorporation of rigid particulate or fibrous reinforcements gives rise to enhanced stiffness and heat distortion resistance, although usually at the expense of impact strength, which can fall dramatically, particularly at high levels of filler addition.[18] Mechanical properties of polymers containing rigid inorganic particles are determined by the size, shape, concentration, and properties of the additive,[18–20] but in particular by its interaction with the surrounding matrix.[18,21–23]

Generally, there is a lack of adhesion between polymer and filler, necessitating the application of modifiers onto the filler surface to enhance interaction at this interface, or through chemical functionalization of the polymer to generate sites for reaction with the filler surface.[24,25] Impact properties depend strongly on effective filler dispersion, with larger agglomerates acting as stress-raising flaws.[20] Also, high aspect ratio filler particles, such as mica, although raising the stiffness of the composite, may reduce its toughness due to stress concentrations at the particle edges. However, under optimum conditions, incorporation of fillers such as calcium carbonate can enhance the ductility of PP by enabling the composite to undergo stable crack propagation through a crack pinning mechanism, rather than by brittle failure.[26,27]

Many fillers are heterogeneous nucleants for PP, influencing not only its temperature and degree of crystallization, but also the nature of the micro-

morphology in the crystalline phase.[28–30] In this context, a correlation was observed between impact strength and melt crystallization temperature in calcium carbonate filled PP, where a higher onset temperature yielded composites with poor toughness.[20,31,32]

Increasingly, PP formulations, containing combinations of filler and elastomer modifiers, are being studied to achieve an optimum balance of stiffness and toughness over a wide temperature range.[33–54] In these so-called ternary phase composites, mechanical properties are determined not only by composition, but also by the phase morphology present, in particular the relative dispersion of additive components. Mechanical properties depend on whether they coexist as separate disperse phases or combine to yield a filler phase encapsulated by elastomer, thereby creating a rubbery interlayer between filler and host polymer.

Thus, of central importance to the study of ternary phase polymer composites containing both rigid filler and rubbery modifier, is the concept of filler encapsulation by elastomer and the effect this has on mechanical properties.

The formation and stability of an encapsulated structure depends on the tendency for filler and rubber to collide, and conditions that favor a morphology with the lowest surface free energy, i.e, when the filler particles are surrounded by an elastomer layer.[37] However, the prevailing shear forces generated during melt processing may result in removal of this layer leading to separate dispersion of filler and rubbery phases. The extent to which this occurs will depend on the relative magnitude of the adhesive

Table II   Melt Flow Characteristics of PP Compositions

Sample	Elastomer Content (Wt %)	Average Torque (N m)	MFI (230°C 10 kg⁻¹)
PP	None	—	7[a]
A	None	55	5.60
E	F-EPR (2.5)	42	4.16
F	F-EPR (5)	45	2.15
G	F-EPR (7.5)	52	1.17
H	EPR (7.5)	52	3.32
C	ENR (7.5)	45	4.79
J	F-EPR/EPR (5/2.5)	45	1.17
K	F-EPR/EPR (2.5/5)	42	2.29
B	None	35	16.8
I	F-EPR (7.5)	45	0.90
D	ENR (7.5)	50	2.77

[a] Measured at 230°C (2.16 kg).

forces between rubber and filler and shear stresses generated within the melt. Hence the morphology and mechanical properties of such ternary phase composites are influenced by the melt rheology of the system, compounding conditions used, and particularly the magnitude of interaction between the components.[55]

From the many experimental studies reported in the literature, which consider the structure and properties of three-phase thermoplastics polymer composites, generally there is support for the concepts outlined above.

For example, in PP/EPDM/calcium carbonate mixtures, surface treatment of the filler resulted in separate dispersion of the modifying phases, whereas
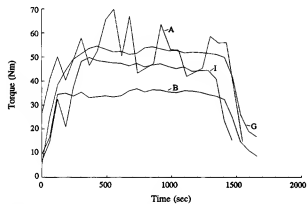

Figure 1   Torque–time curves obtained from Brabender twin-screw extruder during preparation of compounds: A, PP/Mg(OH)₂ (uncoated); B, PP/Mg(OH)₂ (coated); I, PP/Mg(OH)₂ (coated)/F-EPR (7.5%); G, PP/Mg(OH)₂ (uncoated)/F-EPR (7.5%).

encapsulation occurred when unmodified calcium carbonate was used.[36,38]

Various methods were applied to promote filler bonding either to the thermoplastics matrix to achieve separate dispersion of the phases, or to the rubber to encourage filler encapsulation. Using mixtures of PP, EPR, and calcium carbonate or magnesium hydroxide filler, it was shown that PP functionalized with maleic anhydride resulted in separation of filler and elastomer. Introduction of maleinated EPR and nonfunctionalized PP gave filler encapsulation.[56] These distinct morphologies gave significantly different tensile properties and failure mechanisms. In the former case, ductility was increased due to a predominance of shear banding or crazing in the matrix; elastomer encapsulation of the filler encouraged failure by shear yielding by relieving triaxial stresses at the filler surface.

Using calcium carbonate filler, again with functionalized and nonfunctionalized forms of PP and EPR, it was found that rubber encapsulated filler exhibited lower yield stress but higher impact strength than composites made with functionalized matrix.[38]

Multicomponent polyethylene/rubber/filler composites prepared from silane treated forms of silicon dioxide and calcium carbonate powders were also studied.[52–54] The use of silane coupling agents gave improved filler dispersion in the polyethylene matrix and in addition allowed chemical interaction with the maleic anhydride modified EPDM rubber present, thereby creating a rubber encapsulated filler with resulting improvements to impact strength.

Reducing the inherent flammability of PP is normally achieved either by incorporating fire retardant

Table III   Mechanical and Flammability Properties of PP Compositions

Sample	Elastomer Content (Wt %)	Tensile Yield Strength (MPa)	Elongation at Break (%)	Flexural Modulus (MPa)	Izod Impact Strength, Notched (J m⁻¹)	Izod Impact Strength, Notched (kJ m⁻²)	UL94 Rating (at 3-mm Thickness)
Virgin PP	—	22.3	> 600	680	157.1[a]	15.8	HB
A	—	14.9	0.3	2340	19.3	1.90	V-1
E	F-EPR (2.5)	15.4	3.3	1432	32.4	3.23	HB
F	F-EPR (5)	13.1	1.7	918	49.0	4.91	V-1
G	F-EPR (7.5)	12.6	0.9	717	69.9[a]	6.99[a]	V-1
H	EPR (7.5)	12.9	1.5	1321	53.4[a]	5.34[a]	V-1
C	ENR (7.5)	10.7	1.4	1539	12.3	1.23	HB
J	F-EPR/EPR (5/2.5)	12.5	1.8	750	57.0[a]	5.70[a]	V-2
K	F-EPR/EPR (2.5/5)	11.2	0.8	937	49.4[a]	4.94[a]	V-1
B	—	12.9	1.5	1963	48.7[a]	4.86[a]	V-0
I	F-EPR (7.5)	12.6	2.4	818	82.0[a]	8.02[a]	HB
D	ENR (7.5)	10.1	1.3	990	24.9	2.48	V-0

[a] Some specimens did not break during testing.

additives, such as brominated compounds in combination with antimony trioxide synergists, or by using intumescent formulations based on phosphorous-containing materials.[57] However, certain hydrated mineral fillers, in particular aluminum and magnesium hydroxides, offer an attractive alternative because they are acid and halogen free; and in addition to inhibiting polymer ignition, they function as effective smoke suppressants.[58] Of these, magnesium hydroxide is preferred because of its greater thermal stability, which permits its use in thermoplastics (including PP) that are melt processed beyond the decomposition point of aluminum hydroxide.[59] However, to be effective, high filler loadings are necessary, typically in excess of 60% by weight (∼ 37% by volume) when used in PP,

Figure 2   Notched Izod impact strength of ternary phase composites (at 27°C). Compositions given in Table I.
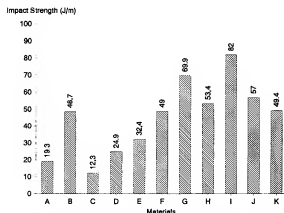
resulting in a significant loss in composite toughness.[60] In common with other mineral fillers, improvements in impact strength can be obtained by treatment of the filler, for example, using silane or titanate surface modifiers.[61] In this regard, fatty acids and their derivatives have been found to be particularly effective, especially when full coverage of the filler surface is ensured.[25] However, combining magnesium hydroxide with a rubber modifier through preparation of a ternary phase composite, offers an alternative route for achieving enhanced toughness, while maintaining fire retardancy and a better overall balance of mechanical properties.

In this article, methods are considered for enhancing the toughness of PP copolymer containing magnesium hydroxide fire-retardant filler using EPR (with and without combined maleic anhydride) and also epoxidized NR (ENR) modifiers. To further influence possible interaction between the component phases, the filler was studied in untreated form and also coated with a fatty acid salt, thereby providing significant differences in filler surface energy and matrix compatibility. Mechanical properties, flammability, and processibility of the compositions are all characterized and phase morphology is analyzed using scanning electron microscopy (SEM) and FTIR.

EXPERIMENTAL

Materials and Formulations

PP copolymer (Profax EP-C 40R), obtained from Titan Himont Polymers (Sdn. Bhd. Malaysia),

was used as the matrix material. This has a melt flow index of 7 g 10 min^{-1} (230°C/2.16 kg). Two EPR modifiers were incorporated into this matrix: Vistalon V878 with melt flow index (MFI) of 3.9 g 10 min^{-1}, (230°C/2.16 kg) and Exxelor VA1803 with MFI of 22 g 10 min^{-1} (230°C/10 kg), both supplied by Exxon Chemicals. The last mentioned grade is a low viscosity amorphous copolymer, reported by the manufacturer to contain 0.7% by weight of grafted maleic anhydride, as determined by FTIR.

Compositions were also formulated containing ENR prepared at the Rubber Research Institute of Malaysia with an epoxide content of 50 mol%. Unmodified magnesium hydroxide fire retardant (Lycal 96HSE) was obtained from Redland Minerals (UK) with a median particle size of 7.7 μm and Brunauer–Emmett–Teller surface area of 18.9 m^2 g^{-1}. This was also supplied in surface treated form, coated with 6% by weight of magnesium stearate, and level shown to give complete surface coverage[25]. This filler has a roughly spherical morphology comprising small aggregated crystallites.

The formulations prepared are listed in Table I. Previous work demonstrated that it is possible to obtain UL94-VO flammability classifications (at 3-mm thickness) with these fillers in PP using 60% by weight additions of magnesium hydroxide.[62] Even though the primary aim of this study was not to optimize ignition resistance, all filler levels were maintained at this value in order to consider the effects of the rubbery modifiers on flammability. In the case of the surface modified magnesium hydroxide grade, an appropriate allowance was made for the presence of chemical treatment.

Preliminary work demonstrated that compound processability diminished markedly when rubber level additions increased much above 7.5% by weight, so this was set as the upper limit for elastomer content.

Compounding and Injection Molding

Compositions were predistributed, then melt compounded in a Brabender Plasticorder PL2000 counterrotating twin-screw extruder, using barrel and die temperatures of 160, 190, and 200°C at a screw speed of 60 rpm. To ensure effective dispersion of the filler and rubber, compounds and the neat control material were extruded twice under these conditions. Screw torque measurements were recorded during the mixing process. The strand extrudate was pelletized, predryed for 24 h at 90°C, and formed into test specimens using a 20-ton

Battenfeld BA200CD Plus injection molding machine, set with barrel temperature profile ranging from 220 to 260°C.

Characterization of Structure, Properties, and Flammability

MFI measurements were conducted according to ASTM D1238 at 230°C using a 10-kg load. Mechanical properties were determined in both tension and flexure, and under impact loadings. Tensile properties were measured on a Lloyd L1000S tensometer at a crosshead speed of 50 mm min^{-1}, in accordance with ASTM D638-89. An IR noncontacting extensometer was employed for determination of elongation at break using a gauge length of 50 mm. Flexural modulus was also measured on the same machine following ASTM D790 using a crosshead speed of 2 mm min^{-1} and specimen span length of 50 mm. Izod impact strength was obtained on notched specimens, using procedures given in ASTM D256-88. Ten specimens were analyzed for each composite. All mechanical testing was carried out at 27°C and 65% relative humidity, in accordance with ISO 291 conditioning procedures for tropical countries.

Dynamic mechanical properties of selected compositions were determined using a Rheometrics RSA II analyzer, under 3-point loading and over a temperature range from −100 to 160°C at a frequency of 6.28 rad s^{-1}.

Flammability was assessed using the UL94 vertical burn test procedure using 3-mm thick test specimens. The phase microstructure of selected materials was studied by SEM on specimens prepared by cooling under liquid nitrogen, then gold coating fracture surfaces. These were examined both as fractured and after exposure to heptane vapor for 4 s to etch the EPR component. Under these conditions, the PP was not affected by the solvent.

Some compositions were also characterized on a Perkin–Elmer 1600 Series FTIR spectrophotometer, specifically to consider possible interaction between the filler and elastomeric phases. For this purpose, neat PP copolymer and EPR rubbers were examined in transmission using compression molded thin films. Multicomponent systems were studied by diffuse reflectance IR spectroscopy (DRIFT), using powder prepared by filing composite moldings, which was then diluted with KBr powder.
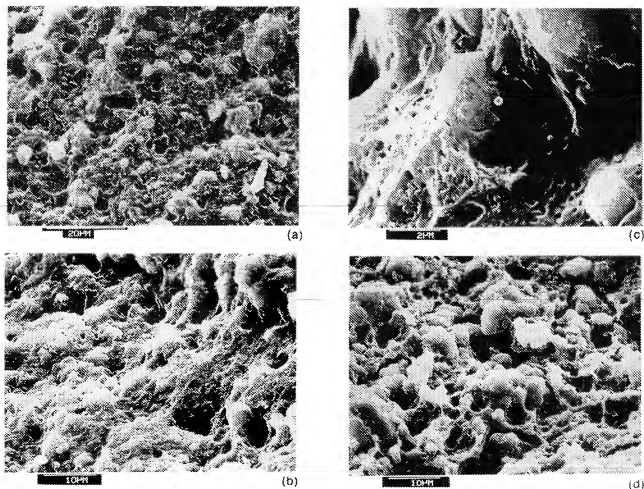
Figure 3 Microstructure of PP compositions: (a) A, PP/Mg(OH)$_2$ (uncoated), unetched; (b,c) H, PP/Mg(OH)$_2$ (uncoated)/EPR (7.5%), etched; (d–f) G, PP/Mg(OH)$_2$ (coated)/F-EPR (7.5%), etched; (g,h) I, PP/Mg(OH)$_2$ (coated)/F-EPR (7.5%), etched.

RESULTS AND DISCUSSION

Melt Flow Properties

Average screw torque values obtained during compound preparation on the Brabender extruder are given in Table II, with typical torque–time curves obtained during processing shown in Figure 1. It is apparent that significant fluctuations in torque occurred with compound A, comprising PP with uncoated filler. However, the corresponding composition containing surface treated magnesium hydroxide, compound B, processed more uniformly and with significantly lower torque requirement. This is consistent with previously reported rheological analysis of these systems that demonstrated that

surface treatment with fatty acid salt resulted in a marked reduction in shear viscosity and interparticle attraction, as determined under low shear dynamic testing conditions using parallel plate rheometry.[63]

In the case of formulations containing 7.5% by weight of functionalized EPR (F-EPR), when uncoated filler was used torque was reduced slightly due to the presence of the rubber (compare compounds G and A). With surface treated filler, however, a further reduction in torque was evident (sample I), but this decrease was far less than when the rubber was absent (compare compounds I and B). Corresponding MFI values for these materials show that, as anticipated, in the two-component system, the effect of the surface coating was to
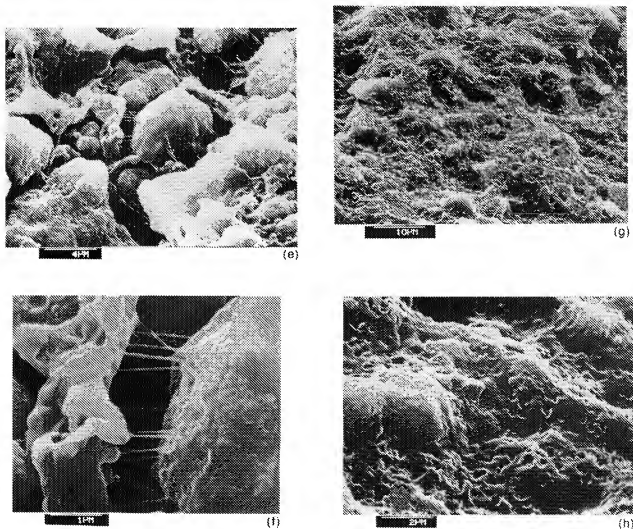
Figure 3 *(Continued from the previous page)*

greatly increase melt flow. However, when only 7.5% by weight of F-EPR was added, the MFI dropped dramatically even when the surface treated filler was used (compare compounds B, G, and I). This unexpected result suggests that either these observations were a reflection on low shear conditions used in the MFI test (an order of magnitude lower than that estimated during twin-screw compounding), or structural changes occurred in the materials that apparently inhibit their flow.

Indeed the latter possibility seems more likely, as the rubber containing materials were noticeably more difficult to injection mold, requiring higher injection pressures to fill the cavity than PP containing only untreated magnesium hydroxide. The type of elastomer modifier and concentration in the ternary phase blend also gives rise to differences in melt

processibility and, in particular, MFI (Table II). Increasing the level of F-EPR (from 2.5 to 7.5% by weight) in PP formulated with uncoated magnesium hydroxide gave a progressive increase in torque during mixing and a corresponding decrease in MFI (samples E, F, and G). At a 7.5% addition level, F-EPR gave a lower MFI than the two other elastomeric modifiers studied. Comparing EPR and F-EPR, the former rubber has higher MFI than the functionalized grade, hence it is possible that their different effects on the rheology of the ternary phase composites is due to chemical interaction between F-EPR and filler, causing increased immobilization of the rubbery phase. This observation is consistent with encapsulation of filler by the rubber.

However, both F-EPR and ENR gave lower MFI values when combined with surface treated mag-
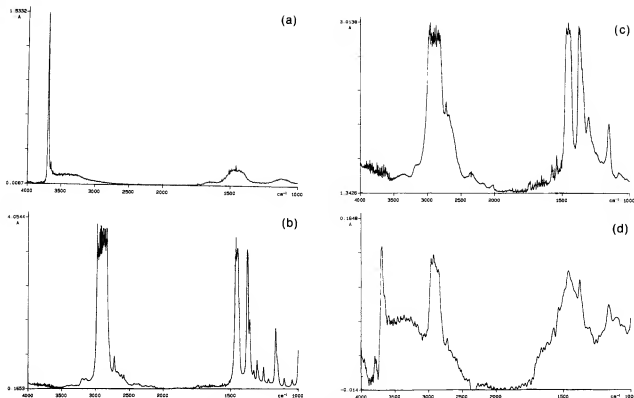
Figure 4 FTIR spectra of PP compositions: (a) magnesium hydroxide (uncoated); (b) polypropylene copolymer; (c) EPR; (d) PP/EPR (7.5 wt %)/magnesium hydroxide (uncoated), (sample H); (e) F-EPR; (f) PP/F-EPR (7.5 wt %)/magnesium hydroxide (uncoated) (sample G).

nesium hydroxide than the uncoated variant, at equivalent percentage additions (compare sample C with D and G with I).

Mechanical Properties and Flammability Resistance

Tensile, flexural, and impact results are presented in Table III. Comparing mechanical properties of neat PP copolymer with compositions containing 60% by weight of magnesium hydroxide filler (samples A and B), confirms the marked fall in tensile strength, impact strength, and in particular, elongation at break, due to the presence of the filler, reported previously using a homopolymer grade of PP.[25,60] Modulus increases due to the stiffening effect of the filler, ameliorated to some extent by the presence of surface treatment.

The exception of ENR, in all cases the presence of the modified interface, leading to a very significant increase in composite toughness. With the exception of ENR, in all cases the presence of the filler.[25,60]

rubber modifier increased impact strength relative to PP filled with uncoated magnesium hydroxide, although significant differences in toughness were observed between the materials tested. Samples C, G, and H are comparable formulations made with untreated magnesium hydroxide, but with different rubber types. Toughness was found to increase in the following order F-EPR > EPR ≫ ENR whereas the opposite trend was found when comparing flexural modulus of these systems, i.e, F-EPR yielded approximately half the modulus of ENR.

In comparable compositions containing mixtures of F-EPR and EPR, results were intermediate between the extremes mentioned above (samples J and K). In ternary phase formulations, higher impact values were obtained when surface treated magnesium hydroxide was used (i.e., samples D and I). With F-EPR, in particular, impact strength increased from 70 to 82 J m⁻¹, with a slight improvement in flexural modulus (samples G and I).

All rubber modified formulations displayed a marked reduction in tensile strength, which was most noticeable when ENR was introduced. The de-
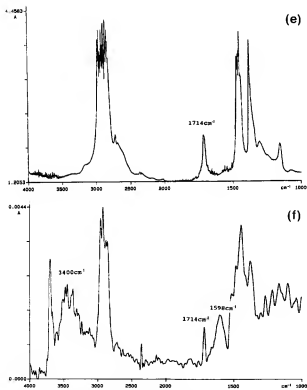
Figure 4 (*Continued from the previous page*)

crease in tensile strength, which accompanies an increase in rubber content (samples E, F, and G), is typical of that seen by other workers in ternary phase composites.[56]

UL94 ratings for 3-mm thick test specimens are shown in Table III. Previous work with the magnesium hydroxide fillers used in this study was undertaken with homopolymer PP, where V-0 classifications are achievable at a 60% by weight filler addition.[62] The present investigation shows that using a copolymer grade of PP, only surface treated filler (TP100) yielded a V-0 rating, uncoated magnesium hydroxide giving only a V-1 value as did many of the ternary phase formulations. This suggests that rubber modification does not seriously impair flammability resistance at addition levels up to 7.5% by weight. However, to ensure a V-0 classification, reformulation to a higher filler content will be necessary.

Characterization of Microstructure

SEM was used to investigate the relative phase morphologies in certain binary and ternary phase composites. To distinguish between the spatial location of rubber and particulate species, samples

were etched with *n*-heptane to remove the elastomeric component.

Figure 3(a) shows that PP copolymer has little affinity for uncoated magnesium hydroxide filler due to large surface energy differences. Interaction between the components is very limited, resulting in extensive particle pull-out from the fracture surface.

In the ternary composite (sample H), in which untreated magnesium hydroxide is combined with 7.5% by weight EPR, it can be seen that after etching, the rubber lies predominantly in the matrix phase in the form of very finely dispersed particles [approximately 0.1–0.5 μm in diameter; Fig. 3(b,c)]. Some of the rubber is present at the filler surface, however, extensive filler encapsulation by the EPR is not apparent. In the same composition, but replacing EPR by the functionalized variant (sample G), a very different microstructure is seen after etching [Fig. 3(d)]. The surface appears highly fragmented, with clear evidence that many of the particles are surrounded by voids or gaps, indicative of large-scale rubber encapsulation. A fine, submicron dispersion of rubber particles also exists in the matrix phase. Figure 3(e) shows an enlarged view of an isolated filler particle from which F-EPR coating has been extracted. However, small fibrils still remain, uniting the filler surface to the surrounding matrix [Fig. 3(f)]. It is clear that these are well bonded to both surfaces, and because this effect was not observed in any of the other compositions studied, they are assumed to be remains of the functionalized rubber phase arising from incomplete solvent extraction.

It is interesting to note that these fibrils appear highly oriented across the interface, suggesting that the rubber has been deformed, perhaps due to shrinkage stresses caused as the semicrystalline PP matrix contracts on cooling from the melt, but is restrained by interaction between filler particles.

However, when F-EPR is combined with surface treated magnesium hydroxide (sample I), a distinctly different morphology is revealed [Fig. 3(g,h)]. The surface texture is much smoother than seen with sample G, and the filler particles remain well wetted by matrix (even after etching) indicating a high degree of compatibility between matrix and filler. There is no indication that filler encapsulation by rubber has occurred; indeed the elastomer phase is uniformly distributed throughout the matrix as finely dispersed droplets, even appearing in this form in the PP coating present on the filler surface.

In summary, these observations demonstrate that by changing the surface properties of the filler or altering the functionality of the elastomeric phase,
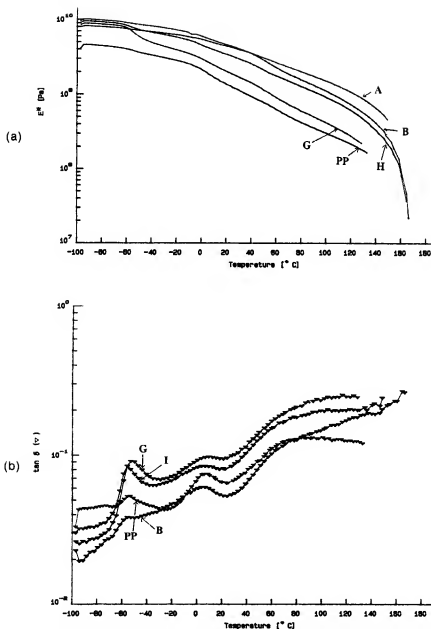
Figure 5 Dynamic mechanical spectra of PP compositions: (a) storage modulus (E^*) and (b) tan δ. PP, PP copolymer; A, PP/Mg(OH)$_2$ (uncoated); B, PP/Mg(OH)$_2$ (coated); G, PP/Mg(OH)$_2$ (uncoated)/F-EPR (7.5%); H, PP/Mg(OH)$_2$ (uncoated)/EPR (7.5%); I, PP/Mg(OH)$_2$ (coated)/F-EPR (7.5%).

the relative interaction between the phases can be strongly influenced. This varies from extensive interaction between untreated filler and maleinized rubber, resulting in extensive filler encapsulation, to almost complete separation of these phases, when the filler surface is effectively isolated from the reactive rubber due to an interlayer of fatty acid salt. As can be seen from the mechanical properties of these materials, the implications of these structural differences on composite toughness are profound.

FTIR spectra of selected ternary phase composites are shown in Figure 4, together with IR absorptions for the constituents in isolation.

The spectrum for the composition made using EPR (sample H) appears as a combination of the three components present with no apparent change
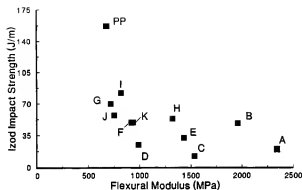
Figure 6 Relationship between notched Izod impact strength and flexural modulus for PP and selected compositions (defined in Table I).

to absorption peaks [Fig. 4(d)]. Comparing spectra for EPR and F-EPR, a large absorption can be seen at 1714 cm^{-1} for the functionalized grade, which is attributed to carboxylic acid. The anhydride form of this modification normally shows two absorptions at 1864 and 1784 cm^{-1},[52] but anhydride moieties are easily hydrolyzed to the acid form, giving rise to the acid absorption shown in Figure 4(e).[64]

Analysis of the ternary phase composite, made using F-EPR and untreated magnesium hydroxide (sample G), is shown in Figure 4(f). It is apparent that in addition to the carboxylic acid absorption at 1714 cm^{-1}, there are peaks evident at 1598 cm^{-1}, associated with carboxylic acid salt formation, and 3400 cm^{-1}, which is characteristic of hydrogen bonding between hydroxyl groups. This provides evidence of an acid–base interaction between the magnesium hydroxide surface and maleic acid functionality, and is consistent with the earlier discussion where it was shown that in this composition, filler encapsulation by rubber is favored.

Dynamic mechanical properties of PP and selected formulations are given in Figure 5 in terms of storage modulus E^* and mechanical damping peaks (tan δ) at temperature from −100 to 160°C. Compared to PP, all filled compositions show an increase in storage modulus over the temperature range of interest [Fig. 5(a)]. The relative values for these binary and ternary phase composites follow the same order as the flexural modulus results reported in Table III.

Tan δ maxima for specific materials are compared in Figure 5(b). The peak at around 6–9°C is caused by the glass transition of PP with a further smaller transition occurring at −53°C attributed to the ethylene component in this copolymer. In ternary phase systems, when 7.5% by weight of rubber is also pres-

ent, the low temperature damping peak is more clearly defined due to the presence of the elastomeric phase. Clearly, there is some overlap in this region between relaxations due to PP copolymer and elastomer. Nevertheless, if maxima are compared from samples containing F-EPR, combined with and without surface treatment (samples I and G), the data show approximately equal intensities of these peaks, but with a slight shift in the low temperature damping peak from −53°C for the sample without surface treatment to −56°C when surface coating is applied. This would be expected if encapsulation in this system had occurred through the inclusion of maleinated EPR, because mobility of the rubber is restricted at the filler interface. The very small difference seen would seem to suggest that either encapsulation with F-EPR is incomplete or the coated elastomer layer is insufficiently thick to exert much effect on the damping behavior of the elastomer phase.[39]

CONCLUSIONS

Methods are reported for influencing the mechanical properties of PP copolymer filled with magnesium hydroxide fire retardant. This may involve preparing composites containing polymer and fully coated filler using fatty acid salt treatment, but also combining PP filler and various rubber modifiers to yield ternary phase composites. In the latter case, both surface coated and untreated fillers were used, together with ENR or EPR (with and without combined maleic anhydride). All PP compounds studied exhibited a marked reduction in tensile properties relative to unfilled PP; however, at a constant filler level, flexural modulus and impact strength could be managed within wide limits by filler surface treatment and through incorporation of rubber modifier. Relative values of these properties are summarized in Figure 6 for the different compositional variants prepared.

It was apparent that surface treatment of the filler resulted in improved wet-out by matrix material and localized deformation of polymer around the filler particles, manifested by stress whitening and giving rise to high toughness. By combining uncoated filler with EPR, however, it was shown that filler particles and rubbery modifier exist as separately dispersed phases and that a further improvement in impact strength can be achieved, accompanied by a significant decline in modulus. F-EPR, on the other hand, was found to give a rubbery interlayer between uncoated filler particles and PP matrix. Evidence for

this encapsulation was provided principally from analysis by SEM and FTIR. PP compositions, made using surface treated magnesium hydroxide and F-EPR, gave the highest toughness of all materials examined, in which there was good interfacial compatibility between filler and matrix and also well-dispersed rubber particles. In this system, no widespread encapsulation of filler by rubber could be observed.

The addition of relatively small amounts of rubbery modifier into magnesium hydroxide filled PP composites gave a significant increase in melt viscosity. UL94 flammability ratings were found to be sensitive to composition. Filler levels greater than 60 wt % are necessary to ensure V-0 classifications.

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